Graft Copolymerization of Methyl Methacrylate Monomer onto Starch and Natural Rubber Latex Initiated by Gamma Irradiation

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ABSTRACT

To obtain the degradable plastic, the graft copolymerization of methyl methacrylate onto starch and natural rubber latex was conducted by a simultaneous irradiation technique. Gamma-ray from cobalt-60 source was used as the initiator. The grafted copolymer of starch-polymethyl methacrylate and the grafted copolymer of natural rubber-polymethyl methacrylate were mixed in the blender, and dried it in the oven. The dried grafted copolymer mixture was then molded using hydraulic press machine. The effect of irradiation dose, composition of the grafted copolymer mixture, film forming condition and recycle effect was evaluated. The parameters observed were tensile strength, gel fraction and soil burial degradability of grafted copolymer mixture. It was found that the tensile strength of grafted copolymer mixture increased by γ-ray irradiation. Increasing of the grafted copolymer of natural rubber-polymethyl methacrylate content, the gel fraction and tensile strength of the grafted copolymer mixture increased. The tensile strength of the grafted copolymer mixture was increased from 18 MPa to 23 MPa after recycled (film forming reprocessed) 3 times. The grafted copolymer mixture was degraded completely after soil buried for 6 months.

INTRODUCTION

Already well known that plastic is valuable material for human life, it's used in an enormous range of products, due to easy to manufacture, versatility and imperviousness to water. They have already displaced many traditional materials, such as wood, metal, glass, and ceramic, in most of their former uses. About 200 billion pounds (100 million tons) of plastics are produced worldwide every year. Plastics are used for packaging, building materials, and virtually every type of consumer product. Past ages of human society have been called the Stone, Bronze, Copper, Iron, and Steel Ages, based on the material that was relied upon the most during that time. Today, the total volume of plastics produced worldwide has surpassed that of steel and continues to increase. Without a doubt, we have entered the Age of Plastics [1].

Some common plastic items include: sunglasses, tooth brushes, super glue, paint brushes, tennis shoes, Frisbees, 2-liter bottles, Honda CRX's, Astroturf, photographs, street signs, pens, automobile paint, video tapes, rubber bands, balloons, bicycle tires, umbrellas, guitar strings, carpeting, shower doors, hearing aids, Scotch Tape, fishing lines, trash bags, and toilet seats [1].

Plastic can be found in everything from clothing to machinery. It is important to understand the nature of plastics, and the consequences of their production and use. Virtually all plastics are made from nonrenewable resources, such as oil, coal or natural gas, which will eventually become exhausted. Beside of valuable materials, Plastics are durable and degrade very slowly; the molecular bonds that make plastic so durable make it equally resistant to natural processes of degradation. Billion tons of plastic has been discarded and may persist for hundreds or even thousands of years. The plastic waste becomes seriously environmental pollution problem [1].

In many countries, plastic recycling programs were used to reduce the plastic waste problem, but it has proven difficult. The biggest problem with plastic recycling is difficult to automate the sorting of plastic waste, and so it is labor intensive. In the other hand, many

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sienceties carried out research on biodegradable plastics that break down with exposure to sunlight, water or dampness, bacteria, enzymes, insect attack are also included as forms of biodegradation or environmental degradation. Some of these modes of degradation will only work if the plastic is exposed at the surface, while other modes will only be effective if certain conditions exist in landfill or composting systems. Starch powder has been mixed with plastic as a filler to allow it to degrade more easily, but it still does not lead to complete breakdown of the plastic. Some researchers have actually genetically engineered bacteria that synthesize a completely biodegradable plastic, but this material, such as Biopol, is expensive at present [2].

To overcome the plastic waste problems, research activities such as blending of linier low density polyethylene with tapioca starch [3] shows that the plastic blended was not degraded completely after soil burried for about 1 year, and low density polyethylene with corn starch shows that the weight loss of plastic blended was only 12,6% after soil burrial for 4 months [4]. Combination of double biodegradable inisiator materials such as starch and natural rubber latex with polymethyl methacrylate was expected to obtain renewable degradable plastic. Studied on the graft copolymerization of methyl methacrylate monomer onto starch and natural rubber latex with gamma irradiation as initiator is presents in this paper. Cassava starch gel, natural rubber latex with 50% of total solid content, and 50% methyl methacrylate monomer solution was used in the experiment. The effect of irradiation dose, composition of copolymerized materials, film forming condition and recycling effect on tensile strength, gel fraction and soil burial degradability of grafted copolymer are reported.

EXPERIMENTAL METHODS

Materials

Cassava starch powder was obtained from the Giant supermarket, Indonesia. Concentrated natural Rubber Latex was obtained from PTP VIII Nusantara, Jalumpang, West Java, Indonesia. Methyl Methacrylate (MMA) monomer pure analysis grade was obtained MERCK product, it was purified before usage. Tween 20 used as emulsionfier. Acetone as solvent used was technical grade.

Preparation of graft copolymer

Cassava starch gel, 50% of methyl methacrylate monomer, and 1% of tween 20 was mixed and irradiated with γ-ray from cobalt-60 source to obtain the grafted copolymer of starch-polymethyl methacrylate. Natural rubber latex with 50% total solid content, 50% of methyl methacrylate monomer, and 1% of tween 20 was mixed and irradiated with γ-ray to obtain the grafted copolymer of natural rubber-polymethyl methacrylate. The grafted copolymer of starch-polymethyl methacrylate and grafted copolymer of natural rubber-polymethyl methacrylate obtained was mixed in a beaker glass with using magnetic stirrer and dried it in the oven. The dried grafted copolymer mixture film was obtained by molded the dried grafted copolymer mixture with using hydraulic press machine. The outline of the graft copolymerization of methyl methacrylate monomer onto starch and natural rubber latex schematically illustrated in Fig. 1.

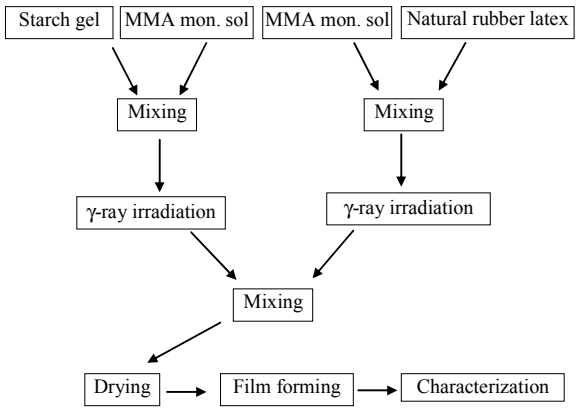

Fig. 1. The out line of the graft copolymerization of methyl methacrylate monomer onto starch and natural rubber latex.

Soil burial degradability of the grafted copolymer

The sample film to be tested was in dried condition and constant weight. The sample film was buried completely into the soil outdoors and left it. The pH of soil was about 7. The tested samples were remove at intervals of time, and it was washed with water repeatedly to remove the remain soil adhered on the sample film, and then the washed sample film dried in the oven to constant weight. The degradability of sample film was indicated from weight loss of sample and calculated gravimetrically.

RESULTS AND DISCUSSION

Effect of γ-irradiation on tensile strength of the grafted copolymer mixture

The effect of γ-ray irradiation on tensile strength of the grafted copolymer mixture containing of 25% starch, 25% natural rubber and 50% polymethyl methacrylate illustrated in Fig. 2. The tensile strength of the grafted copolymer mixture increased up to maximum level, then decreasing with increasing of irradiation dose. The maximum tensile strength was achieved at irradiation dose of 5 kGy. Increasing of tensile strength of the grafted copolymer mixture related with chemical bonding between the grafted copolymer molecules [5], mathematically illustrated by the equation as follow,

$$\sigma = RT\nu\,[(\lambda) - (1/\lambda^2)]$$

where σ is modulus of copolymer, ν is density of crosslinked molecules, R and T are gas constant and absolute temperature, and λ is the elongation value. The modulus of copolymer will increased with increasing density of crosslinked molecules. While the decreasing of tensile strength of the grafted copolymer mixture is due to degradation of polymethyl methacrylate under radiation.

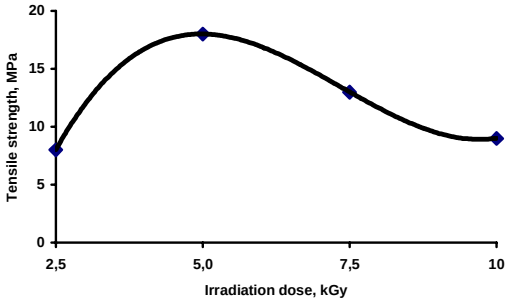

Fig. 2. Effect of γ- irradiation on tensile strength of the grafted copolymer mixture.

The chemical bonding of the grafted copolymer is related with reaction mechanism of graft copolymerization, where free radical reaction involved [6]. The first stage of free radical reaction was interaction of γ-ray with water to form free radical (R•). At the second stage, the free radical formed was then initiate free radical reaction with monomer (M) and polymer (P) to form new free radical of monomer (M•) and polymer (P•). While at the third stage, propagation of free radical formed by reaction of new free radical with monomer (RM_{n+1}•) and polymer (RP_{n+1}•). At the last stage of free radical reaction, recombination between free radicals occured to form homopolymer (R-Mn+m-R), grafted copolymer (RP-M_{n+m}-R) and crosslinked polymer (RP-PR). Schematically the reaction mechanism of the graft copolymerization of monomer onto polymer illustrated as follow,

$$H_2O \rightarrow R\bullet\ (H\bullet \text{ or } OH\bullet) \quad (1)$$
$$R\bullet + M\bullet \rightarrow RM\bullet \quad (2)$$
$$R\bullet + P\bullet \rightarrow RP\bullet \quad (2)$$
$$RM\bullet + n\,M\bullet \rightarrow RM_{n+1}\bullet \quad (3a)$$
$$RP\bullet + nM\bullet \rightarrow RPMn\bullet \quad (3b)$$
$$RM_n\bullet + RM_m\bullet \rightarrow R\text{-}M_{n+m}\text{-}R \text{ (homopolymer)} \quad (4)$$
$$RPM_n\bullet + RM_m\bullet \rightarrow RP\text{-}M_{n+m}\text{-}R \text{ (graft copolymer)} \quad (4)$$
$$RP\bullet + RP\bullet \rightarrow RP\text{-}PR \text{ (cross linked polymer)} \quad (4)$$

Effect of composition of the grafted copolymer mixture

The effect of composition of the grafted copolymer of starch-polymethyl methacrylate and natural rubber-polymethyl methacrylate on the tensile strength and gel fraction of the grafted copolymer mixture illustrated in Table 1. The experiment results as shown in Table 1, the graft copolymerization irradiation dose of starch-polymethyl methacrylate and natural rubber-polymethyl methacrylate was 10 kGy and the film forming condition of the grafted copolymer mixture was carried out at 150°C for 3 minutes and pressed by 20 MPa.

Table 1. The effect of composition of the graft copolymer starch- polymethyl methacrylate and the graft natural rubber-polymethyl methacrylate on tensile strength and gel fraction of grafted copolymer mixture.

Composition of starch-g-PMMA/Natural rubber-g-PMMA, gram	Gel fraction, %	Tensile strength, MPa
200/25	59	6
200/50	60	8
200/100	77	9
200/200	79	10

According to Table 1, the gel fraction and tensile strength of the grafted copolymer mixture were 59% and 6 MPa, 60% and 8 MPa, 77% and 9 MPa, 79% and 10 MPa, respectively at the composition of grafted copolymer starch-polymethyl methacrylate/grafted copolymer natural rubber-polymethyl methacrylate were 200/25, 200/50, 200/100 and 200/200 respectively. The increasing of gel fraction and tensile strength of the grafted copolymer mixture with increasing of grafted natural rubber-polymethyl methacrylate was because of natural rubber easy to dissolve in methyl

methacrylate monomer and easy to crossliked by γ radiation. It means with increasing of natural rubber molecule number in the grafted copolymer mixture, will increasing of the crosslinked molecule number. With increasing crosslinked molecules number, the grafted copolymer mixture molecule will difficult to dissolve in solvent and difficult to break when it strengthen, it means increasing in gel fraction and tensile strength of the grafted copolymer mixture.

Effect of film forming condition

The effect of temperature and pressure of film forming (molding) on tensile strength of the grafted copolymer mixture illustrated in Table 2. The experiment results as shown in Table 2, the the grafted copolymer mixture was containing of 25% starch, 25% natural rubber and 50% polymethyl methacrylate, radiation copolymerization dose was 5 kGy, while the molding time was 3 minutes. According to table 2, the appropriate film forming condition was at temperature 170°C and pressure 20 MPa respectively. The increasing molding temperature at 20 MPa pressure, and increasing the pressure molding at a temperature of 170°C has affected increasing in tensile strength of grafted copolymer mixture at temperatures up to a maximum level of 170°C and pressure of 20 MPa.

Table 2. The Effect of temperature and pressure of molding on tensile strength of the grafted copolymer mixture.

Temperature of molding, °C	Pressure of molding, MPa	Tensile strength, MPa
130	20	11
150	20	16
170	**20**	**18**
190	20	14
170	10	14
170	15	15
170	**20**	**18**
170	25	16

While increasing molding temperature above 170°C and pressures above 20 MPa, resulting in reduced tensile strength of grafted copolymer mixture. The increasing tensile strength of grafted copolymer mixture was due to increasing in number of crosslinked molecules, and decreasing tensile strength of the grafted copolymer was due to excess the crosslinked molecules number and the grafted copolymer mixture become brittle [7].

Effect of recycling on tensile strength of the graft copolymer mixture

Plastic recycling is the process of recovering scrap or waste plastics and reprocessing the material into useful products, sometimes completely different in form from their original state. For instance, this could mean melting down soft drink bottles and then casting them as plastic chairs and tables. Typically a plastic is not recycled into the same type of plastic, and products made from recycled plastics are often not recyclable [8]. The effect of recycling on the tensile strength of the grafted copolymer mixture containing of 25% starch, 25% natural rubber, and 50% polymethyl methacrylate illustrated in Table 3. The irradiation of graft copolymerization was 5 kGy. According to Table 3, the tensile strength of the grafted copolymer mixture was increased from 18 MPa to 23 MPa after recycling 3 times, then decreased to 20 MPa after recycling 4 time.

Table 3. The effect of recycling on the tensile strength of the grafted copolymer mixture.

Recycling, time	Tensile strength, MPa
1	18
2	22
3	23
4	20

The increasing tensile strength of the grafted copolymer mixture was due to molecular regrouping induced on rearrangement molecular of the grafted copolymer, the distance between molecules regrouping become narrower. While, decreasing tensile strength of the grafted copolymer mixture because of chain fracture occurred.

Soil burial degradability

The experimental results of soil burial degradability of the grafted copolymer mixture illustrated in Table 4, where the ph of the soil was 7. According to table 4, the grafted copolymer mixture was degraded slowly after soil burial, while it degraded completely after soil buried for 6 months. The *Aspergillus niger* microorganism enhanced degradation of grafted copolymer mixture by attacked to cleave the polymer chain, thus yielding fragments to further degradation in environment because of their low molecular weight [9].

Table 4. Effect of soil burial duration on weight loss of the grafted copolymer mixture. The copolymer containing of 25% starch, 25% natural rubber and 50% polymethyl methacrylate, and the radiation polymerization dose was 5 kGy.

Duration of soil burial, month	Weight loss, %
1	18
3	85
6	100

CONCLUSIONS

The degradable plastic could be obtained by gamma radiation graft copolymerization of methyl methacrylate monomer onto starch and natural rubber latex. The grafted natural rubber-polymethyl methacrylate enhanced the gel fraction and tensile strength of the grafted copolymer mixture. The appropriate molding temperature and pressure of the grafted copolymer mixture were 170°C and 20 MPa respectively. The maximum tensile strength of grafted copolymer mixture was found 18 MPa with the composition of starch 25%, natural rubber 25% and polymethyl methacrylate 50%, at 5 kGy gamma irradiation dose. Recycling up to 3 times were enhanced tensile strength of the grafted copolymer mixture. The grafted copolymer mixture was degraded completely by soil burial for 6 months.

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